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PRE-TERRESTRIAL OXIDATION PRODUCTS IN CARBONACEOUS METEORITES IDENTIFIED BY MÖSSBAUER SPECTROSCOPY

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Introduction. The occurrence of ferric-bearing assemblages, comprising phyllosilicates, oxide hydroxides and magnetite, in carbonaceous chondrites (hereafter abbreviated as CC) indicates that these meteorites underwent pre-terrestrial sub-aqueous oxidation reactions. Although several analytical studies of CC, have been reported [e.g.,1,2], the poor crystallinity of matrix phases makes it very difficult to estimate the modal mineralogy and proportions of Fe^{3+} and Fe^{2+} in these meteorites [2]. Early studies of Mössbauer spectra of meteorites at room temperature demonstrated that this technique may provide quantitative information on iron-bearing phases in CC [e.g.,3,4]. In a recent study of ureilites, for example, major proportions of metallic Fe and nanophase goethite were identified in these carbonaceous achondrites [5]. The metallic Fe occurs mostly as sub-microscopic inclusions in forsteritic rims where they have formed by carbon-induced reduction of Fe^{2+} cations in olivine grains in contact with the carbonaceous matrix [6]. The cryptocrystallinity of the metallic Fe inclusions renders the metal extremely vulnerable to oxidation so that nanophase ferric oxides (i.e. "rust") occur in all ureilites, including specimens collected as *falls*. The vulnerability of olivines in ureilites to such redox reactions suggested that other pre-terrestrial oxidation processes might be elucidated in CC, the olivines in which have undergone reactions producing serpentines, magnetite and poorly crystalline phases such as ferrihydrite and tochilinite [e.g.,2,7,8]. Reported here are results of a Mössbauer spectral study of a suite of CC demonstrating that a variety of ferrous and ferric-bearing phases may be distinguished in different classes of this meteorite-type.

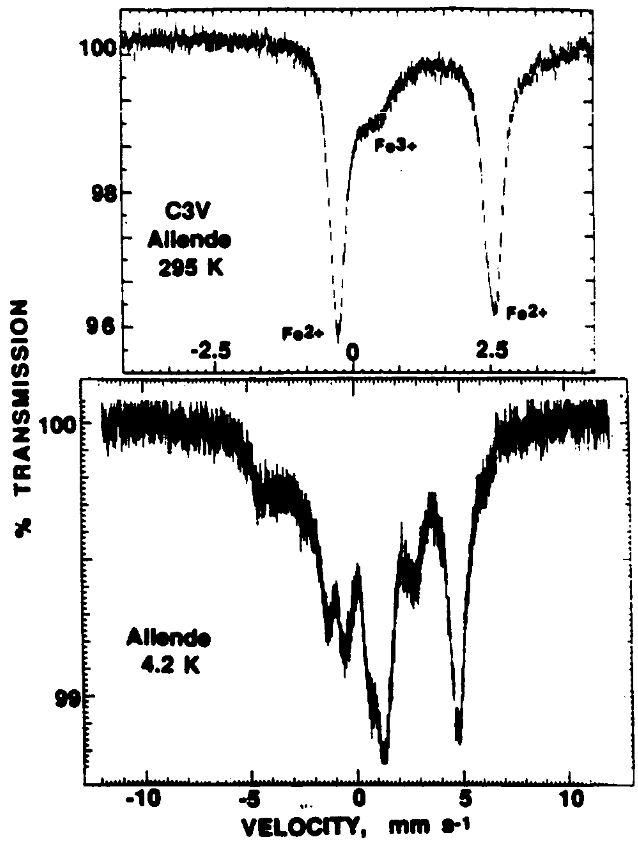
Carbonaceous Chondrite Specimens. Samples of several CC catalogued as *falls* were obtained from the Harvard Mineralogical Museum Collection, and included: Orgueil (CI); Murchison, Murray, Cold Bokkeveld and Renazzo (CM); Allende (CV3); Warrenton (CO3); Karoonda (C5); and the *find* Coolidge (C4). Specimens acquired from the Antarctic Meteorite Collection, including some powdered (P) samples, comprised: ALH 83100(P) and MAC 88107 (CM); ALHA 83108 and LEW 85332 (C3); EET 87256(P) and ALHA 85002(P) (C4); EET 87860(P) (C5); and LEW 87009(P) (C6). Experimental details for measuring Mössbauer spectra of meteorites are described elsewhere [9].

Results. Room temperature Mössbauer spectra of several CC have been published previously [3,4,10-12]. In our investigation, systemmatic measurements were made of several CC petrologic types at both 295 K and 4.2 K. Trends observed in these spectra include:

(1) The relatively simple 295 K spectrum of Allende (CV3) (**Fig. 1**) consists of Fe^{2+} and Fe^{3+} quadrupole doublets alone representing mainly olivine and phyllosilicates, respectively, and with $\%Fe^{3+}$/total Fe = approx. 10%. The 4.2 K spectrum of Allende is dominated by peaks from magnetically ordered Fe^{2+} ions in olivine. No magnetic ferric phase is present in Allende.

(2) The spectrum of Cold Bokkeveld (CM) at 295 K also consists of Fe^{2+} and Fe^{3+} doublets alone, but with comparable intensities (**Fig. 2**). In the 4.2 K spectrum of this and other CM meteorites, however. the Fe^{2+} doublet of ferroan serpentine remains while magnetic ordering of Fe^{3+} has occurred, indicating the presence cronstedtite [12,13] possessing a magnetic ordering temperature of ≤8 K [14]. The iron hydroxysulfide mineral tochilinite, which is particularly abundant in CM CC [2], does not magnetically order at 4.2K, by analogy with related mackinawite [15], and is recognized by peaks centered near 0.2 mm/s. The relative proportions of these secondary minerals, which formed during aqueous alteration on the meteorite parent body, differ in the Mossbauer spectra of other CM CC meteorites (Murchison, Murray, ALH 83100).

(3) The 295 K spectrum of Karoonda (C4) contains the Fe^{2+} olivine doublet and a much weaker Fe^{3+} doublet than Allende, as well as the characteristic magnetic hyperfine spectrum of magnetite which constitutes about 15% of the iron modal mineralogy (**Fig. 3**). The relative intensities of paired-peaks in the magnetite spectrum are not in the ratio 1:2, however, indicating that this oxide in Karoonda and in other thermally metamorphosed CC is an oxidized magnetite departing from $Fe^{2}Fe^{3+}{}_{2}O_4$ stoichiometry. The 4.2 K spectrum of Karoonda is dominated by magnetite and magnetically-ordered Fe^{2+} in olivine. Similar 295 K and 4.2 K spectra were obtained for other C4, C5 and C6 specimens studied (i.e. ALHA 85002, EETA 87860, EET 87526, LEW 87009). Coolidge (found in 1937) contains no magnetite; instead, its 4.2K spectrum contains broadened peaks attributed to terrestrial nanophase goethite.



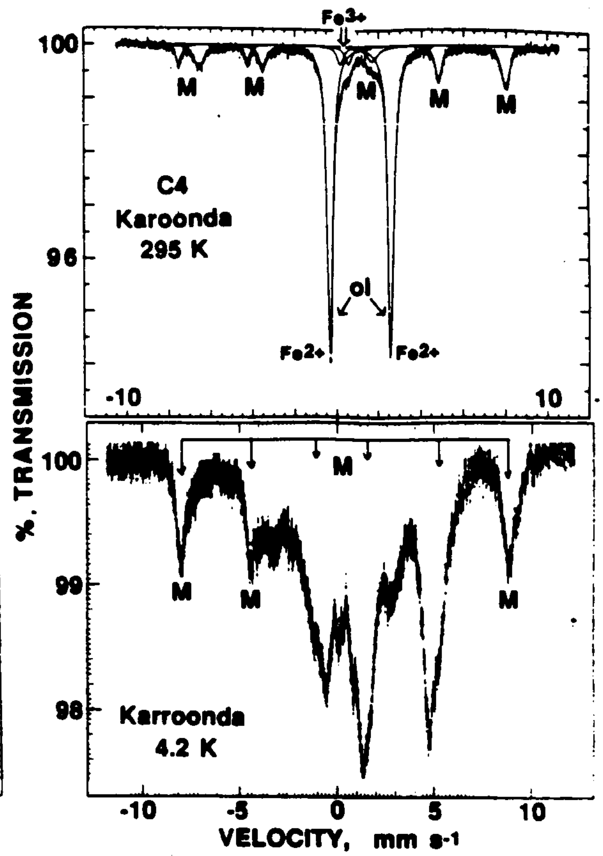


Figure 1. Mössbauer spectra of the Allende meteorite. The spectra of this carbonaceous chondrite are dominated by olivine, Fe^{2+} ions in which are magnetically ordered in the 4.2 K spectrum.

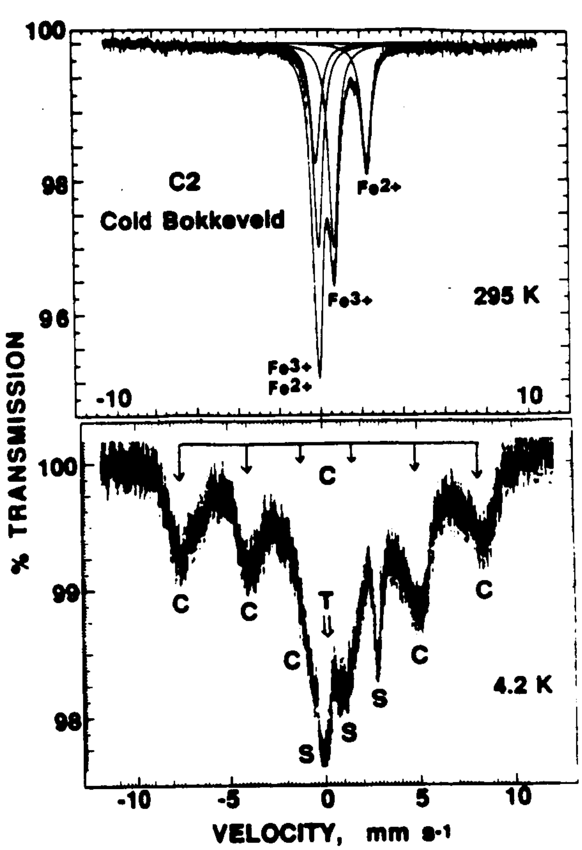
Figure 2. Mössbauer spectra of the Karoonda meteorite. Olivine (ol) and non-stoichiometric (slightly oxidized) magnetite (M) occur in this and other thermally metamorphosed carbonaceous chondrites.

(4) The spectrum of Orgueil (CI) at 295 K resembles previously published spectra of this CC [3,16], and consists of an intense Fe^{3+} doublet, a very weak Fe^{2+} doublet and the magnetic hyperfine profile of non-stoichiometric magnetite (Fig. 4). At 4.2 K, the Fe^{3+} doublet has collapsed to a sextet, the peaks of which flank and broaden the magnetite peaks. This behavior is indicative of ferrihydrite [16], recently identified [8] as the the superparamagnetic phase proposed in Orgueil [17,18]. The spectra of Orgueil are thus consistent with the occurrence of magnetite, ferrihydrite, Fe^{3+} serpentine (cronstedtite) and Fe^{2+} serpentine in the matrix [8]. Similar Mossbauer spectra were obtained for other CI meteorites (Ivuna, Tonk, Alais).

(5) The Mössbauer spectra of other CC not illustrated here revealed that Renazzo has major metallic Fe, minor magnetite, and Fe^{2+} and Fe^{3+} doublets of comparable intensities which do not order magnetically at 4.2 K. Metallic Fe but no magnetite occurs in ALHA 83108 (C3) and LEW 85332 (CO3) together with nanophase goethite, apparently formed by oxidative weathering in Antarctica, by analogy with ordinary chondrites [9]

Ureilite Mössbauer Spectra. Following previous discoveries [5] by Mössbauer spectroscopy of high modal proportions of metallic Fe and the presence of ferric oxides in all ureilites studied, as well as further examples of pigeonite Fe^{2+} exceeding olivine Fe^{2+}, additional ureilites were acquired for further spectral measurements at 4.2K to confirm these trends.

(1) Major amounts of metallic iron were determined in Goalpara, ALHA 82106, ALHA 82130, and LEW 85440. Minor amounts of Fe occur in MAC 88177 and EETA 83309, in which carbonaceous matrix is either negligible or localized in discrete areas not surrounding olivine grains.



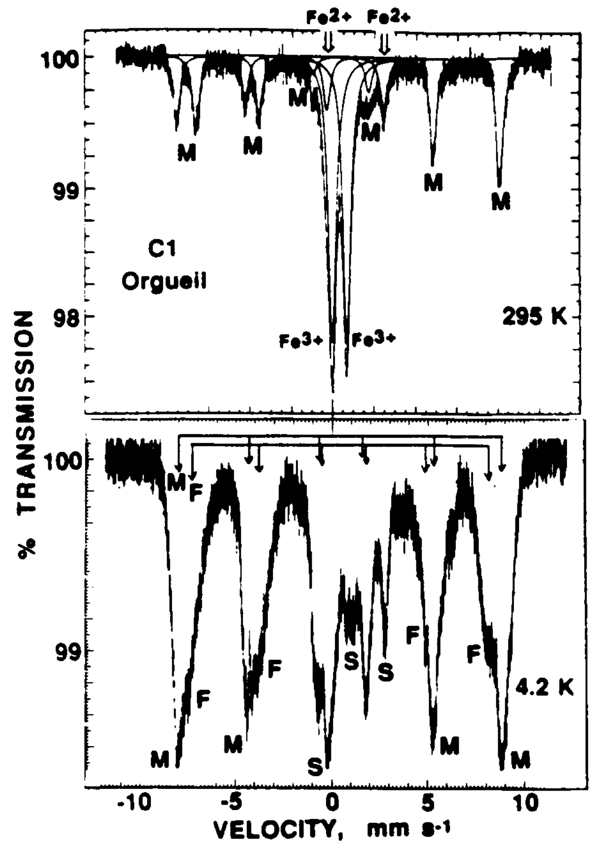


Figure 3. Mössbauer spectra of the Cold Bokkeveld meteorite. In 4.2 K spectra of this and other CM carbonaceous chondrites, features attributed to tochilinite (T), Fe^{2+}-Fe^{3+} serpentine (S) and magnetically ordered cronstedtite (C) may be distinguished.

Figure 4. Mössbauer spectra of the Orgueil meteorite. In this and other CI carbonaceous chondrites, non-stoichiometric magnetite (M) is present together with Fe^{2+}-Fe^{2+}-bearing phyllosilicates (S) and ferrihydrite (F) which becomes magnetically ordered by 4.2 K.

(2) The modal proportion of Fe^{2+} olivine exceeds Fe^{2+} pigeonite in Goalpara, EETA 83225, LEW 85440 and MAC 88177. The Fe^{2+} modal proportions are reversed in ALHA 82106 and ALHA 82130, with pyroxene > olivine. Pyroxene is a very minor constituent of EETA 83309.
(3) Each of these ureilites contains significant to high proportions of ferric oxides, including Goalpara, the freshness of which led to the speculation that it was recovered soon after an unrecorded *fall.* [19]. The FeOOH content is least in MAC 88177, the ureilite with negligible carbonaceous matrix.

These observations confirm the mechanism of carbon-induced reduction of Fe^{2+} in olivinein ureilites [6] and the vulnerability of the sub-microscopic metallic Fe inclusions to rusting, presumably upon exposure to Earth's atmosphere.

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